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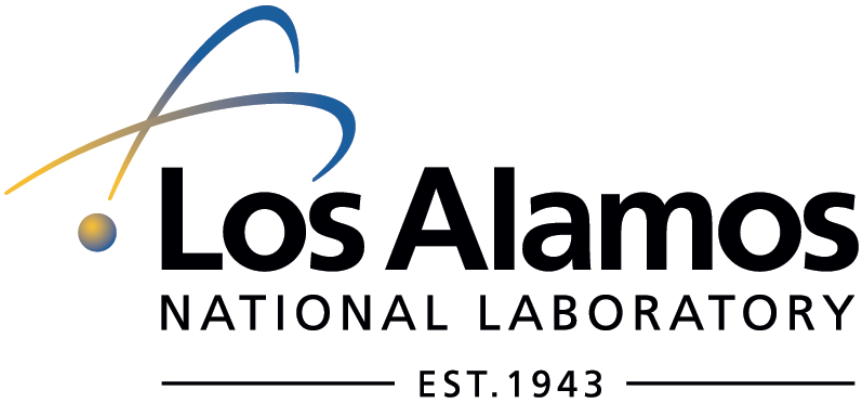

Aging and Lifetimes

Silicone Elastomers with Novel Modified Filler for Increased Radiation Resistance

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Executive Summary

Radiation induced chemical aging behavior in filled silicone elastomers results in a decreased mechanical performance over time. This report describes chemical methodologies to reduce radiation aging via a surface-modified filler. Four different modified fillers were incorporated into a silicone polymer matrix and subjected to accelerated radiation aging. Fillers modified with aryl group such as phenyl, styrl, and napthyl functionality should improve the radiation aging behavior of the composite material. A series of analytical methodologies were applied to determine the efficacy of the modified filler approach as a mitigation strategy for radiation damage. The results support that phenyl and napthyl modified fillers mitigated radiation damage when compared to control samples and samples with hexyl (non-aryl) modified filler.

Background

Performance engineering materials, such as filled silicone elastomers, when exposed to radiation often experience failure as a result of radiation-induced aging phenomena. Radiation aging in filled silicone elastomers is often attributed to continued crosslinking due to radicals formed by radiation induced damage. [1] This continued crosslinking is manifest as undesirable higher compression set for aged materials. Strategies that limit this continued crosslinking should minimize compression set. According to literature reports [2],[3], polymer/filler interactions play a major role in radiation induced aging of filled silicone elastomers; radiation induced crosslinking directly on the filler surface with the polymer has been observed.[3,4,5] The addition of aryl (mainly phenyl) functionality within the polymer backbone is one chemical strategy that has been exploited to impart radiation resistance to these materials. The resonant structure of aryl groups can delocalize the energy imparted by ionizing radiation. Aryl-functionalized filler has not been previously explored. By placing aryl functionality at the polymer/filler interface we are purposefully adding chemical functionality (aryl) that imparts "radiation hardening" at that interface. This report summarizes the synthesis of surface-modified fillers, compounding the fillers into a silicone polymer, radiation aging of these samples, and post radiation exposure analysis compared to control (unirradiated) samples. Future work includes working to integrate these fillers into existing, 3D printable formulations. This effort seeks to uniquely contribute to DOE-complex wide silicone research while being cognizant of the far more mature resin development work done at other sites. The molecules chosen for filler functionalization are shown in Figure 1. Hexyltrimethoxysilane (HTMS), phenyltrimethoxysilane (PTMS), styrltrimethoxysilane (STMS), and napthyltrimethoxysilane (NTMS) each react with the silanol groups on the surface of silica (Figure 2). In this series of experiments HTMS acts as a control as it has no aryl character and is not expected to contribute to rad hardening. PTMS, STMS, and NTMS each have aryl character and are expected to contribute to rad hardening; the vinyl group of STMS can also crosslink with the polymer so both covalent and entanglement polymer/filler interactions will be probed.

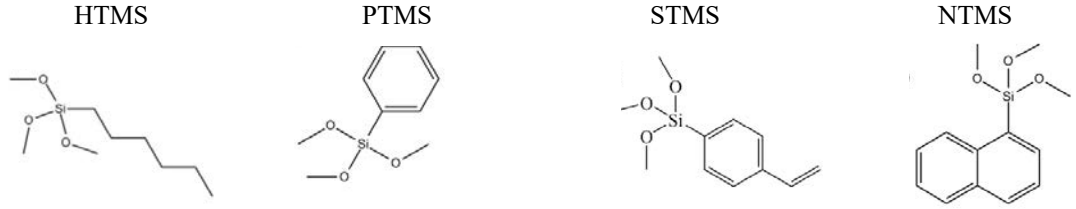

Figure 1: Various silane filler functionalities investigated in this series of experiments; left to right HTMS, PTMS, STMS, and NTMS.

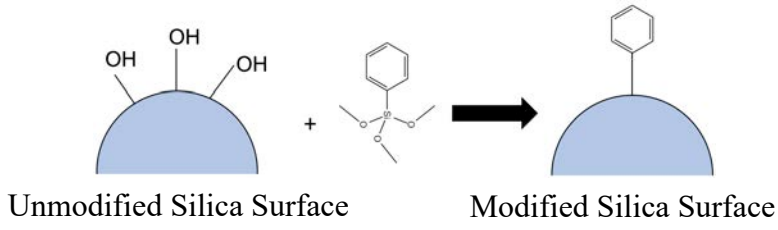

Figure 2: Schematic of filler functionalization showing PTMS.

Methods

Functionalization of Filler

The functionalization chemistry of silanes on silica surfaces is well studied and facile. To accomplish homogenous mixing at a relevant scale for the project, a pilot scale V blender (Torpac Promixer) was purchased. This methodology is a production friendly, scalable technology for powder mixing and homogenization used in pharmaceuticals. Filler functionalization involves spray coating the silica filler with a solution of the silane, homogenizing the coating of the filler in the V blender, and heating the coated filler in an oven to complete the reaction. The silane is dissolved in ethanol (25% by weight silane). An example of HTMS modified filler is as follows:

The ratio of silica filler to silane surface modifier was chosen based on recommendations and a formulation calculator tool from Gelest, the manufacturer of both the silane and the filler. The calculator takes into account characteristics of both the filler and the silane. Following these recommendations, 11.42 grams of silane is used for 20 grams of unmodified filler. The HTMS silane is dissolved in ethanol (25 wt% silane) under constant stirring at 500 rpm for 30 minutes.

Figure 3: Torpac ProMixer V blender used for filler functionalization.

The large 750 mL shell of the V blender is filled with 20 g of unmodified filler. The silane in ethanol solution is spray coated onto the filler in three equal aliquots and mixed for 5 minutes between each addition. Once the entire solution is sprayed on the filler, the filler is mixed in the blender for 1 hour. The modified filler is then heated in an oven at 110 °C for 2 hours. Finally, the modified filler is sieved with a 250 micron mesh to reduce clumping.

Compounding of Silicones

The polymer formulation used for this study is loosely based upon the formulation of Sylgard 184. We have modified some aspects of it to ease formulation. For example, the part A and part B of the formulation is mixed 1:1 by weight instead of 1:10, while maintaining the important vinyl:methyhydro ratio for reactivity. The formulation used for this study is presented in Table 1.

Part A	Component	Wt%
DMS-V31, Gelest	Vinyl term PDMS (28K MW)	76.9
SIT7298.0, Gelest	Tetrakis(trimethysiloxy)silane	3
SIP6829.2, Gelest	Pt carbonyl cyclovinylmethylsiloxane complex	0.01
E51406, Sigma Aldrich	1-Ethynyl-1-cyclohexanol	0.1
SIS6960, Gelest	Amorphous Silica Filler	20
	Total	100
Part B	**Component**	**Wt%**
HMS053, Gelest	MethylHydro-PDMS (20-25K MW, 4-6% H)	50
DMS-V31, Gelest	Vinyl term PDMS (28K MW)	27
SIT7900.0, Gelest	1,3,5,7-tetravinyl-1,3,5,7,-tetramethylcyclotetrasiloxane	3
SIS6960, Gelest	Amorphous Silica Filler	20
	Total	100

Table 1: An example formulation of the silicone polymer matrix that was used for the rad aging study.

When incorporating the modified filler into the polymer matrix, the following mixing procedure was used: The resin is mixed in two parts, Part A and Part B, in a 1:1 ratio to ensure the SiH to vinyl ratio to be approximately 4:1. Part A and Part B initially are mixed separately in a DAC 150.1 FVZ-K Speedmixer (shown in Figure 4) for 30 seconds at 3500 rpm three times. When the resin is ready to be molded, Part A and B are mixed under vacuum for 30 seconds at 3500 rpm two times. The resin is then transferred into a syringe for dispensing. The resin filled syringe is then centrifuged for 5 minutes at 2000 rpm to remove air bubbles.

Figure 4: Speedmixer for blending silica fillers and silicone polymers. Speedmixer employs unique Dual Asymmetric Centrifuge technology for faster, more uniform mixing.

Radiation Exposure

Sample container materials, sample quantity, sample size, aging gas environment, total radiation dose, radiation dose rate, and post exposure analysis techniques were parameters considered for this study. Radiation exposure experiments were carried out in sample cans that were constructed with an aluminum body, conflat flange, a valve, a pressure relief valve, and a pressure gauge as shown in Figure 5. For sample geometry, Mat Celina of SNL was consulted for his expertise in Diffusion Limited Oxidation (DLO). DLO takes place in air-aged samples;

this phenomena can lead to polymers which have experienced surface oxidation from air, but for which the inner portion of the sample does not experience this same ambient environment.[6] These sample inhomogeneities are to be avoided to eliminate the effects of DLO on analytical results. A maximum allowable sample thickness was calculated using the following equation:

$$L_{90} = \sqrt{\frac{\alpha_c \; \mathrm{p} \; \mathrm{P}_{ox}}{(\beta + 1)\; \phi_O \; I \;\; \rho \; 22400}}$$

Where, L_{90} is the maximum allowable thickness, $\alpha_c/(\beta+1)$ is a constant (5.26 was used) that represents the oxidation rate dependence on partial pressure, p is the initial pressure inside the aging canister, P_{ox} is the oxygen permeability coefficient of the material, ϕ_O is the oxygen consumption rate, I is the dose rate, and ρ is the material density. A maximum allowable sample thickness of 4.7 mm was calculated to avoid DLO phenomena and ensure a homogeneous sample. Button molds were fabricated to mold samples of a nominal sample thickness of 4 mm and diameter of 13 mm (Figure 5). The molds were filled with resin, clamped to closure, cured for 2 hours at 150 °C, removed from the molds, and finally post cured at 150 °C for 4 hours. Silicone button samples were aged in both a compressed and uncompressed state. The compression fixtures were designed to compress the button samples 25 % as shown in Figure 5. Each of the four modified fillers were tested (HTMS, PTMS, STMS, and NTMS) in triplicate under dry air conditions with one additional set of STMS buttons aged in argon. The samples were chosen to be aged in dry air as we believe this will be a rigorous environment to induce oxidative aging in a short amount of time. All samples were exposed to a total of 12.5 MRad at a dose rate of 13 rad/s at the Gamma Irradiation Facility (GIF) at Sandia National Laboratory using a ^{60}Co source. The total dose and dose rate were chosen after reviewing the polymer rad aging literature[3,4,5] and represent a moderate amount of aging.

Figure 5: (left to right) Cans that held samples, compression fixtures to compress buttons 25%, and the button mold to form the button samples.

Analytical Methods

The post exposure analytical plan consists of TGA, DSC, FTIR, solvent swell, and hardness testing. Button mass and height were also recorded before and after exposure. Compression set was calculated from the button heights. TGA and DSC will probe thermal degradation of samples. FTIR will probe chemical changes. Solvent swell probes polymer crosslinking and polymer/filler interactions. All analytical results were compared to baseline results collected on samples unexposed to radiation.

Button Height, Mass, and Hardness

Button height was measured using a Mitutoyo Absolute Digimatic Height Gage. The height of each sample was measured 10 times and averaged. Button heights before and after were used to calculate compression set.

Button mass was measured using a Mettler Toledo analytical balance (ME403E). Hardness was measured by a Rex Durometer 1600 type A. Hardness was measured 5 times and averaged.

Compression Set

Compression Set (C_s) is defined by the following equation:

$$C_s = \frac{t_0 - t_i}{t_0 - t_s} * 100$$

Where t_0 is the initial thickness, t_i is the final thickness and t_s is the shim thickness. Considering the equation, accurate part height determination is critical for accurate compression set values. When viscoelastic materials (such as filled silicones) are compressed they can undergo both physical and chemical stresses. The physical stresses often recover over a period of time and therefore are not related to permanent deformations from chemical stresses that may be induced by true aging phenomena (i.e., changes in cross linking, chain scission, etc.)

A small study was initiated to optimize the conditions to relax physical stress and most accurately measure part height of compressed parts for this study.[7] Nine NTMS-modified filler buttons were aged at 25% compression for 70 hours at 72°C; roughly following ASTM D-395. Button height was measured prior to aging. Following the brief aging, the buttons were removed from the compression rigs and treated according to the following: 1) 3 buttons were relaxed at room temperature, 2) 3 buttons were allowed to relax at 45°C and 3) buttons were allowed to relax at 75°C. The goal was to find a minimal time and temperature at which the parts reach a steady state so as not to induce additional thermal aging during relaxation. Figure 6 shows the percentage of original height as a function of time for the three temperatures studied. It can be seen that after 60 minutes a steady state is reached for each temperature with greater recovery observed at higher temperatures. Therefore, for this study, part height will be measured 60 minutes after the parts have been released from compression, with no additional heat treatment.

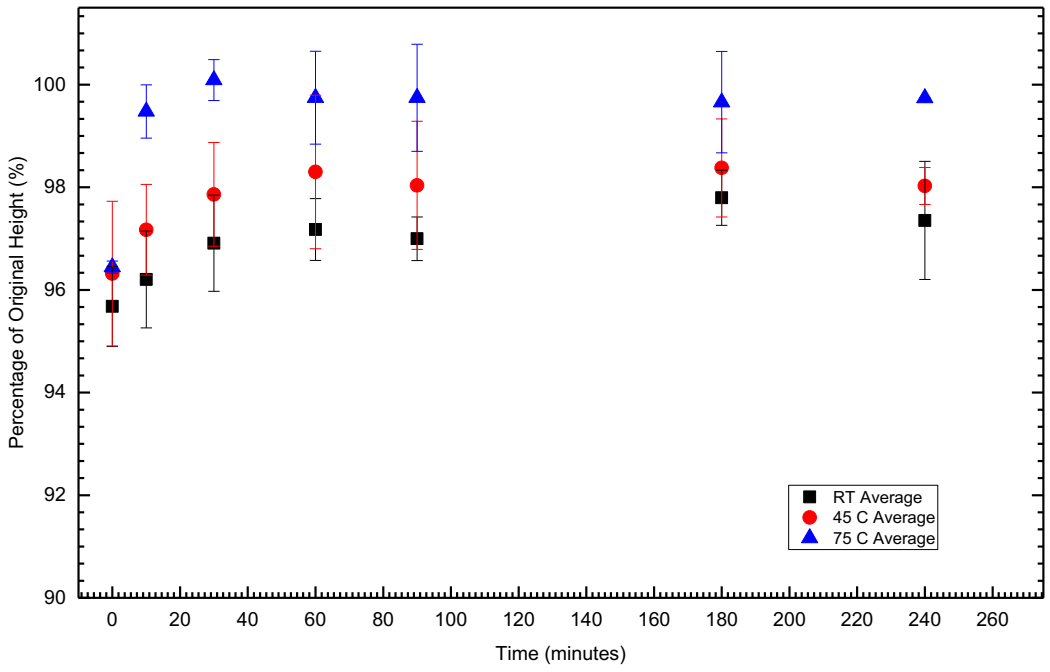

Figure 6. Percentage of original height as a function of time for optimizing relaxation time and temperature for compression aged buttons.

Thermogravimetric Analysis (TGA)

TGA thermograms were collected using a Thermal Analysis TA-Q-5500. Sample mass was approximately 10-25 mg. Samples were ramped at 10 °C/min to 1000 °C under a nitrogen atmosphere. Thermogram analysis was accomplished using TA-Universal Analysis software.

Fourier-Transform Infrared Spectroscopy (FTIR)

FTIR spectra were collected using a Nicolet iS50 FTIR spectrometer with an ATR diamond sample cell. Spectra were collected at 32 scans over a range of 400-4000 cm^{-1}.

Differential Scanning Calorimetry (DSC)

DSC thermograms were collected using a Thermal Analysis TA-Q-20-A. Samples mass was approximately 5 to 15 mg. The heating program for conventional DSC measurements was carried out as follows: 1) Samples were equilibrated at 35 °C, 2) Ramped to -20 °C at 10 °C/min, 3) Ramped to -130 °C at 5 °C/min, 4) Held at -130 °C for 5 minutes, 5) Ramped to 100 °C at 10 °C/min. Thermogram analysis was accomplished using TA-Universal Analysis software.

Solvent Swell

Solvent swell experiments for filled silicone elastomers are well developed.[3,8,9] Samples were analyzed by the following steps: 1) the initial dry mass of the sample was recorded, 2) Samples were immersed in ~30 mL of toluene (Fisher Scientific, 99% purity), 3) Samples soaked in toluene for approximately 13 days until saturation was reached; during this period samples were weighed periodically by removing the sample from the solvent and lightly dried, 4) Once the samples had reached saturation, approximately 5 mL of ammonium hydroxide (~28-30 %) was added to the toluene and the samples were allowed to swell while being weighed periodically until once again reaching saturation. Once saturation was reached the samples were allowed to dry for 10 days and final masses were measured.

Results and Discussion

Functionalization of Filler

We characterized each filler via TGA and IR. The low temperature weight loss TGA data indicates approximately how much filler is on the surface compared to the unmodified filler. This low temperature loss can be converted into a molar loss for each filler. TGA data (Table 2) shows approximately similar amounts of surface coverage for each silane. Overall the data suggests the amount of modifier increases as MW and structural rigidity of the modifier increase.

Filler	Average wt% loss @ 300°C	Average wt% loss @ 625°C	Average Moles on Surface
HTMS	95.40 +/- 2.02	89.13 +/- 2.57	0.0406 +/- 0.0178
PTMS	92.31 +/- 3.68	89.34 +/- 4.23	0.0731 +/- 0.350
STMS	85.53 +/- 12.74	80.07 +/- 10.73	0.1103 +/- 0.0971
NTMS	74.86 +/- 0.06	71.72 +/- 0.06	0.1619 +/- 0.0004

Table 2: TGA data showing approximate similar surface coverages for functionalized HTMS, PTMS, STMS, and NTMS.

IR spectroscopy shows each silane has successfully modified the filler surface (Figures 7-10). In each case the spectra of modified, unmodified, and surface modifier are compared to show the treated materials share the chemical makeup of the modifier. Three unique samples were taken from each batch of modified filler showing excellent homogeneity is achieved during processing. Each of these silanes have unique IR signatures to indicate success of surface functionalization. The IR spectra of each filler show retention of the modifier signatures as compared to the spectra of the modifier (green trace) and unmodified filler (pink trace). Note the alky stretches around 3000 cm^{-1} in the HTMS modified filler and the aryl C-C stretches around 1400 cm^{-1} in the PTMS, STMS, and NTMS modified filler.

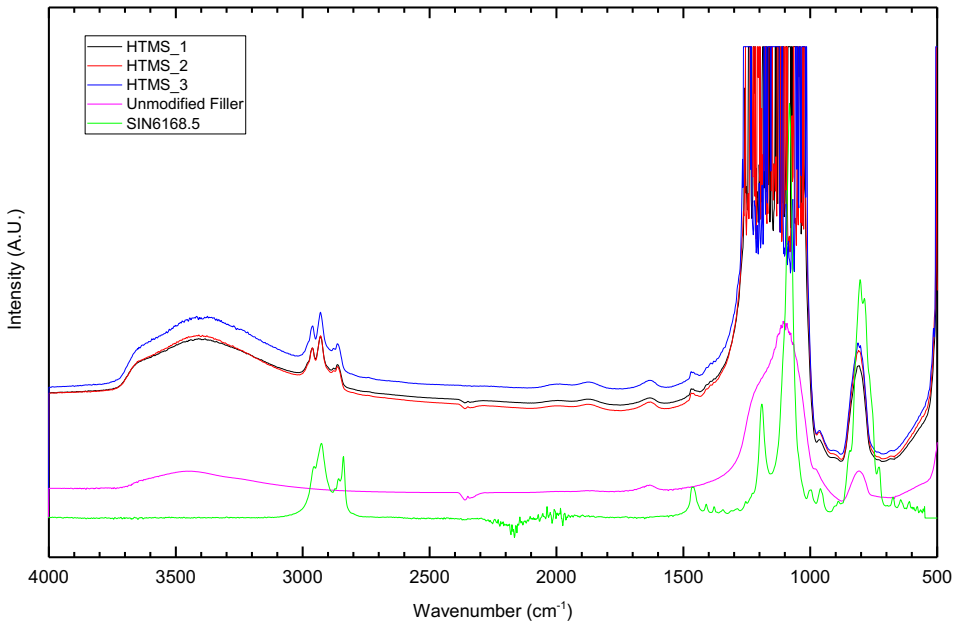

Figure 7: FTIR spectra of HTMS modified silica filler.

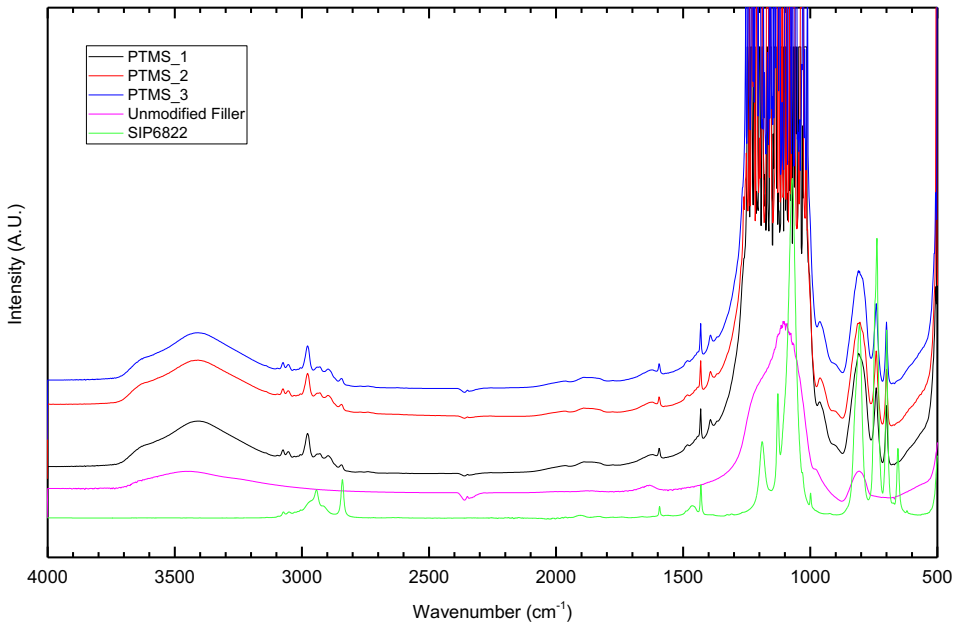

Figure 8: FTIR spectra of PTMS modified silica filler.

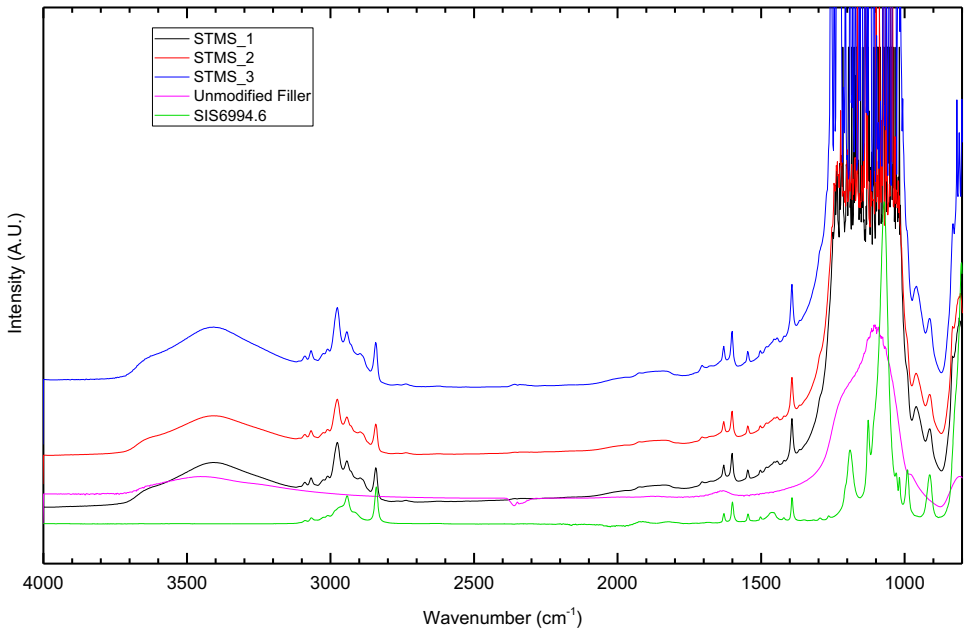

Figure 9: FTIR spectra of STMS modified silica filler.

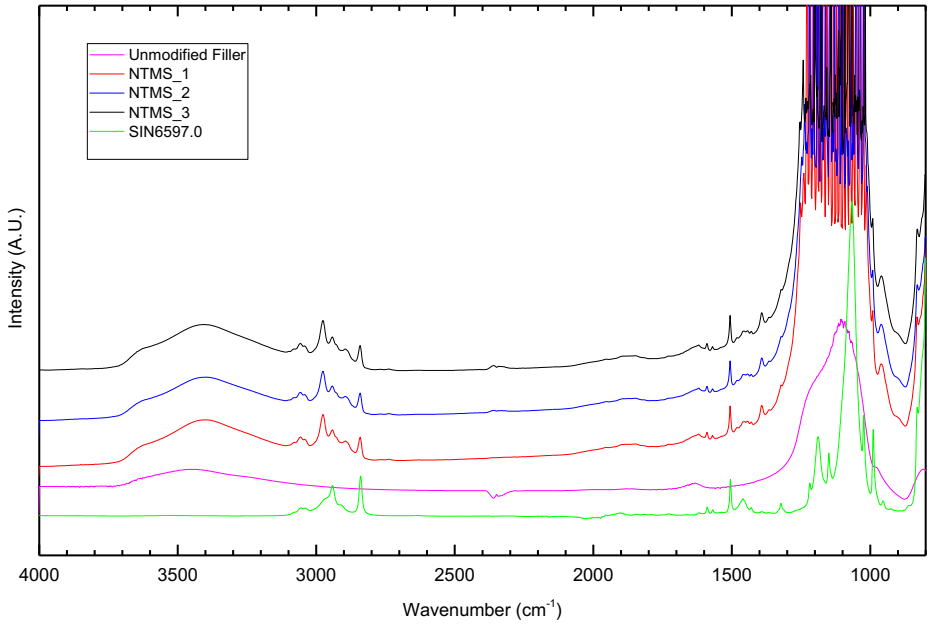

Figure 10: FTIR spectra of NTMS modified silica filler.

Post Exposure Analytical

Mass, hardness, compression set, TGA, DSC, solvent swell, and FTIR studies on control samples (uncompressed with no radiation exposure) were completed and compared to samples that were radiation exposed under 25 % compression and radiation exposed without compression. The data is presented in tabulated form in the text and category plots in Appendix A for ease of comparison. All FTIR data is presented in Appendix B. In all cases, the average and standard deviation values presented are from the analysis of at least three unique samples. The results for control (uncompressed, non-radiation exposed) compression set is based on replicate analysis of one sample and the error presented was calculated by standard propagation of error measurements of the sample height. For TGA, DSC, and IR analysis an exterior or interior portion of samples were used for analysis to confirm sample homogeneity.

Button Mass and Hardness

For all silicone/filler combinations and experimental conditions the mass of all button samples remained constant showing virtually no change in mass (Figure A-1, Table 3). This lack of change suggests that all filler variants are stable and no catastrophic radiolysis degradation was observed. Sample masses were also constant for samples aged in argon and air. Hardness values show a similar trend (Figure A-2, Table 4) and did not change as a result of radiation exposure in any environment. HTMS buttons had the highest durometer of 64 and PTMS buttons had the lowest durometer of 46. Changes in durometer have been observed in radiation aging studies of filled silicones but for silicones with higher durometer (> 50) little change was observed under 12.5 Mrad.[10]

Δ mass	**Radiation Exposed Compressed**		**Radiation Exposed Uncompressed**	
Filler Type	Average	Std. Dev.	Average	Std. Dev.
HTMS	-0.001	0.001	-0.001	0.001
PTMS	0.000	0.001	0.001	0.001
STMS	0.001	0.001	0.002	0.001
STMS Argon	-0.003	0.008	0.002	0.002
NTMS	-0.002	0.004	0.000	0.001

Table 3: Change in button mass comparing filler type with radiation exposed samples under compression and radiation samples not held under compression.

Hardness	**Control**		**Radiation Exposed Compressed**		**Radiation Exposed Uncompressed**	
Filler Type	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.
HTMS	64	8	64	1	64	1
PTMS	46	1	48	1	60	8
STMS	59	4	60	2	56	9
STMS Argon	--	--	62	2	52	7
NTMS	49	1	49	1	49	1

Table 4: Hardness values (Shore A) comparing filler type with control to radiation exposed samples under compression and radiation samples not held under compression.

Compression Set

Compression set (Figure A-3, Table 5) results indicate that filler modified with aryl groups provided an added benefit compared to fillers that were not modified with aryl groups. The compression set of HTMS samples increased from 2.8 % to 14.5 % after radiation exposure; whereas the compression set of PTMS and NTMS samples showed no statistically significant increase in compression set within one standard deviation. STMS samples aged in argon or air did show an increase in compression set. This is likely due to continued crosslinking of the STMS filler. Stoichiometry of vinyl groups on the filler surface were not taken into account during formulation; rather we prioritized keeping filler content constant at 20 weight percent. During the cure, methylhydro groups in part B of the formulation can crosslink with vinyl groups of both the polymer and the filler surface leaving some vinyl groups unreacted, leading to increased compression set.

Compression Set	**Control**		**Radiation Exposed Compressed**	
Filler Type	Average	Std. Dev.	Average	Std. Dev.
HTMS	2.8	1.8	14.5	3.2
PTMS	10.3	3.9	16.5	3.0
STMS	6.3	1.8	18.8	3.1
STMS Argon	--	--	19.6	7.6
NTMS	10.4	4.3	10.1	3.9

Table 5: Compression set (%) values comparing filler type with control to radiation exposed samples under compression and radiation samples not held under compression.

Thermogravimetric Analysis (TGA)

TGA results indicate that filler modified with aryl groups provided an added benefit compared to fillers that were not modified with aryl groups. TGA characterizes a materials thermal decomposition with data plotted as weight loss as a function of temperature. A typical TGA thermogram is presented in Figure 11.

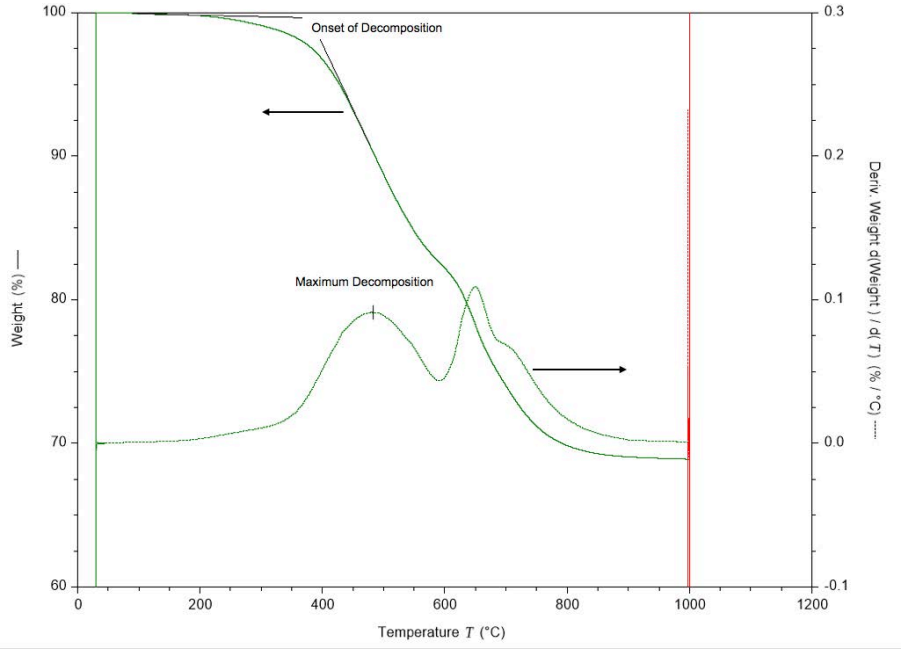

Figure 11: A typical TGA thermogram for the modified filler study.

The temperature at the onset of decomposition and the temperature at the maximum rate of decomposition are important metrics for this study. These metrics are indicative of the extent of crosslinking of a polymer network. Higher temperatures indicate a more crosslinked network while lower temperatures indicate a less crosslinked network. Radiation induced degradation is explained by continued crosslinking, therefore we expect shifts to higher temperatures for both the onset of decomposition and the maximum rate of decomposition for radiation damaged samples. In materials formulated without aryl-functionalized filler (HTMS) an increase in these temperatures is observed for radiation exposed samples compared to control samples. Furthermore, for samples with aryl-functionalized filler (PTMS, STMS, NTMS) these temperatures remain constant (Figures A-4 and A-5, Tables 6 and 7). The magnitudes of the onset of decomposition temperature is similar for all systems studied, but it is the change within each system between radiation exposed (compressed or uncompressed) and control samples that tests the efficacy of aryl-modified fillers in mitigating radiation damage. There were no differences in TGA results between radiation exposed samples that were compressed or uncompressed. STMS samples aged in argon behaved similarly to those aged in dry air suggesting aging atmosphere does not lead to changes in TGA data. The TGA data of STMS samples shows no change after radiation exposure. This, along with the observations of the compression set data suggest that most of the unreacted vinyl groups reside on the filler surface. Figure A-6 and Table 8 show the residue weight remaining after thermal decomposition. In cleanly decomposing filled polymer systems this weight can be interpreted as filler content. Silicones do not decompose cleanly but leave a glassy residue which is a combination of filler and decomposition products of the polymer. There is no observable change in the residue at 950 °C.

Onset of Decomposition Temperature (°C)	Control		Radiation Exposed Compressed		Radiation Exposed Uncompressed	
Filler Type	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.
HTMS	359.46	3.25	385.93	14.73	377.49	6.64
PTMS	383.23	4.35	381.96	1.87	382.51	4.37
STMS	399.21	7.59	403.49	4.86	400.08	6.65
STMS_Ar	-	-	398.39	5.34	404.97	9.23
NTMS	378.99	6.30	378.90	3.93	378.50	1.38

Table 6: TGA results; onset of decomposition temperature (°C) comparing filler type with control to radiation exposed samples under compression and radiation samples not held under compression.

Temperature of Maximum Rate of Decomposition (°C)	Control		Radiation Exposed Compressed		Radiation Exposed Uncompressed	
Filler Type	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.
HTMS	450.10	6.18	478.70	15.72	473.32	13.35
PTMS	468.58	9.79	461.98	2.65	463.36	2.13
STMS	475.44	5.90	471.97	9.37	472.18	4.95
STMS_Ar	-	-	474.20	10.98	475.79	10.11
NTMS	442.07	4.47	443.04	4.05	443.73	0.21

Table 7: TGA results; temperature of maximum rate of decomposition (°C) comparing filler type with control to radiation exposed samples under compression and radiation samples not held under compression.

Weight Percent at 950°C (%)	Control		Radiation Exposed Compressed		Radiation Exposed Uncompressed	
Filler Type	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.
HTMS	71.47	1.12	68.81	1.75	68.90	1.05
PTMS	68.16	2.63	68.52	1.06	67.31	1.63
STMS	71.80	1.14	71.27	0.53	71.63	1.05
STMS_Ar	-	-	72.05	0.28	70.51	1.37
NTMS	70.62	1.03	70.13	0.10	69.65	1.68

Table 8: TGA results; weight percent at 950°C (%) comparing filler type with control to radiation exposed samples under compression and radiation samples not held under compression.

Differential Scanning Calorimetry (DSC)

DSC measures the melting and crystallization properties of a material. DSC results (Figures A-7 through A-10; Tables 9 through 14) show small changes in only STMS samples aged in argon and NTMS samples. A typical DSC thermagram is presented in Figure 12, highlighting the crystallization and melting temperatures and the associated enthalpy of each transition. Irradiated STMS samples aged in argon had slightly lower crystallization temperatures for both compressed and uncompressed states compared to non-irradiated controls (Tables 9 and 10). Similarly, STMS samples aged in argon had lower enthalpies of crystallization (ΔH_c) and formation (ΔH_f) for compressed and uncompressed samples compared to controls (Tables 11 and 14). These enthalpic differences suggest STMS samples aged in

argon decreased in crystallinity. A decrease in crystallinity measured by DSC has been observed in other relevant studies.[4] The decrease in crystallinity is also evidence of an increase in crosslinking that would disrupt segmental diffusion therefore limiting crystallinity. The difference between STMS samples aged in dry air versus argon gas could suggest longer lived radicals created by radiolysis in inert atmospheres compared to air aged samples. An increase in the enthalpy of formation (ΔH_f) was observed for NTMS

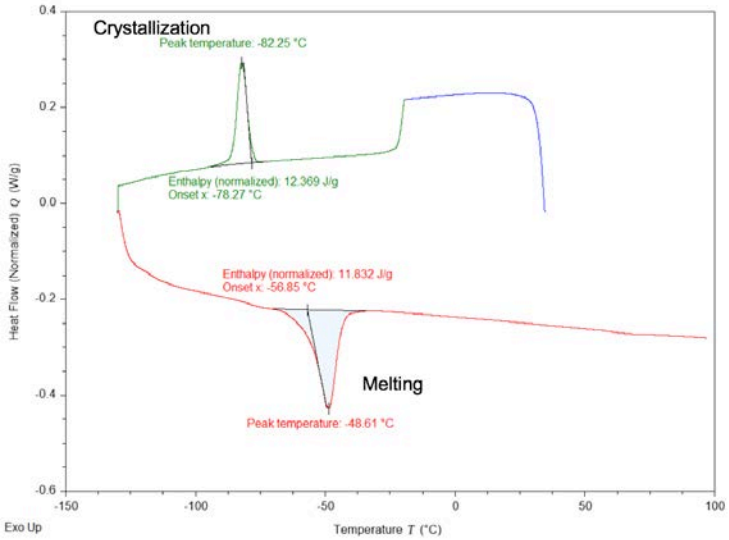

Figure 12: A typical DSC thermogram for the modified filler study.

samples (Table 14) indicating a slight increase in crystallinity. The enthalpy of crystallization (ΔH_c) for NTMS samples shows a similar trend, with higher enthalpies observed for compressed and uncompressed radiation exposed samples compared to non-radiation exposed samples. It is possible that the highly conjugated NTMS system filler facilitates an enhancement in crystallization. Large changes in the melting and crystallization behavior would suggest changes in the crystalline domains of the polymer system. In general, these changes are rather small but provide a metric in aging studies.

Crystallinity Onset Temperature (°C)	**Control**		**Radiation Exposed Compressed**		**Radiation Exposed Uncompressed**	
Filler Type	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.
HTMS	-56.41	0.24	-56.61	0.10	-56.56	0.38
PTMS	-52.65	0.43	-53.88	0.38	-52.99	0.94
STMS	-52.54	0.43	-52.75	0.53	-52.58	0.59
STMS_Ar	-	-	-52.49	0.42	-52.49	0.18
NTMS	-54.36	0.56	-54.05	0.70	-54.33	0.50

Table 9: DSC results; crystallinity onset temperature (°C) comparing filler type with control to radiation exposed samples under compression and radiation samples not held under compression.

Crystallinity Maximum Temperature (°C)	Control		Radiation Exposed Compressed		Radiation Exposed Uncompressed	
Filler Type	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.
HTMS	-48.44	0.49	-48.38	0.31	-48.83	0.24
PTMS	-46.79	0.14	-47.22	0.21	-46.54	0.52
STMS	-45.97	0.31	-45.90	0.38	-46.22	0.28
STMS_Ar	-	-	-45.76	0.54	-45.55	0.07
NTMS	-47.29	0.27	-47.20	0.37	-47.57	0.26

Table 10: DSC results; crystallinity maximum temperature (°C) comparing filler type with control to radiation exposed samples under compression and radiation samples not held under compression.

ΔH_c (J/g)	Control		Radiation Exposed Compressed		Radiation Exposed Uncompressed	
Filler Type	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.
HTMS	11.31	0.15	10.97	0.30	10.90	0.32
PTMS	13.66	0.14	13.50	0.31	12.97	0.53
STMS	13.76	0.29	13.27	0.45	13.61	0.08
STMS_Ar	-	-	12.04	0.22	12.11	0.27
NTMS	12.08	0.51	12.90	0.37	12.88	0.38

Table 11: DSC results; ΔH_c (J/g) comparing filler type with control to radiation exposed samples under compression and radiation samples not held under compression.

Melting Onset Temperature (°C)	Control		Radiation Exposed Compressed		Radiation Exposed Uncompressed	
Filler Type	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.
HTMS	-78.19	0.24	-78.19	0.49	-77.46	1.43
PTMS	-73.62	1.12	-75.89	0.41	-74.27	1.90
STMS	-69.91	1.07	-72.15	1.55	-71.16	0.88
STMS_Ar	-	-	-72.41	0.58	-71.57	0.20
NTMS	-75.64	0.96	-75.52	1.92	-76.27	1.48

Table 12: DSC results; melting onset temperature (°C) comparing filler type with control to radiation exposed samples under compression and radiation samples not held under compression.

Melting Maximum Temperature (°C)	Control		Radiation Exposed Compressed		Radiation Exposed Uncompressed	
Filler Type	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.
HTMS	-82.09	0.20	-82.15	0.60	-81.53	1.34
PTMS	-77.24	1.45	-80.23	0.90	-78.37	2.28
STMS	-76.43	0.31	-77.99	1.56	-76.82	0.93
STMS_Ar	-	-	-78.11	0.73	-78.56	0.51
NTMS	-81.78	1.21	-79.77	2.45	-80.43	1.77

Table 13: DSC results; melting maximum temperature (°C) comparing filler type with control to radiation exposed samples under compression and radiation samples not held under compression.

ΔH_f (J/g)	Control		Radiation Exposed Compressed		Radiation Exposed Uncompressed	
Filler Type	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.
HTMS	12.29	0.08	12.13	0.20	11.93	0.43
PTMS	14.86	0.23	14.22	0.40	13.81	0.41
STMS	14.37	0.79	14.06	0.23	14.23	0.21
STMS_Ar	-	-	12.87	0.64	12.51	0.27
NTMS	12.57	0.46	13.72	0.35	13.97	0.47

Table 14: DSC results; ΔH_f (J/g) comparing filler type with control to radiation exposed samples under compression and radiation samples not held under compression.

Fourier-Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy probes the chemical structure of the polymer. All FTIR data are presented in Appendix B, comparing radiation exposed samples to control samples. Full spectra are presented along with detailed plots of the C=C region (1350-1500 cm^{-1}). For all silicone/filler combinations and experimental conditions (radiation exposed compressed and radiation exposed uncompressed) the FTIR data shows no changes in material chemical structure after radiation exposure. The spectra of these samples are complicated due to spectral overlap from many species in the polymer and filler. Therefore, subtle changes may not be observable or may be below the detection limit of the instrument. Detail plots of the C=C region show no changes.

Solvent Swell

Solvent swell experiments probe the degree of crosslinking of a polymer. The more a polymer swells, the less crosslinked the polymer network. In this study, a two solvent approach was taken. Button samples were first submerged in toluene to swell the polymer network. Once an equilibrium mass was observed, ammonium hydroxide was added to disrupt the filler surface silanol/polymer hydrogen bonding interactions. Equilibrium for the first swell was determined to occur at day 9 and confirmed at day 13. Equilibrium for the second swell was determined to occur at day 23 and confirmed at day 29. Overall, solvent swell studies show little to no difference in samples that were exposed to radiation compared to control samples (Figures A-11 through A-14). Relative weight as a function of time shows the swelling process in a qualitative manor. In most cases there is good agreement between the relative weight of radiation exposed and control buttons, indicating little change in the polymer network (first swelling step) and the polymer filler interface (second swelling step). The second swell involving the addition of ammonium hydroxide to the toluene has been shown to be dependent upon the concentration of surface silanols.[8] The siloxane modifiers used in this study replace surface silanols therefore this swell observation may not be as effective for a surface modified filler. The HTMS samples show slightly lower relative weights for both radiation exposed compressed and uncompressed samples relative to controls. This indicates continued cross linking in the case of the radiation exposed samples. PTMS and STMS samples showed no statistical change, but standard deviations in the data were large. NTMS samples showed no change suggesting NTMS samples were the most robust and consistent performing.

Future Outlook

These data support the hypothesis that modified fillers such as phenyl and napthyl aid in mitigating radiation induced damage in filled silicone elastomers. Silicones containing styrl modified filler may show similar or enhanced mitigation compared to phenyl or napthyl modified fillers, but the formulation must be more carefully considered with regards to reactive group stoichiometry. Future work will include a variable dose study to provide a fuller perspective on radiation aging behavior. Incorporation of these fillers in developed DIW formulations and aging of additively manufactured silicone materials would be warranted.

Acknowledgements

The authors would like to thank Aging and Lifetime Program Sponsors Thomas Zocco and Charles Hills for funding this work, Mat Celina of Sandia National Laboratory for helpful discussions when considering Diffusion Limited Oxidation, and Maryla Wasiolek and Don Hanson of Sandia National Laboratory for assistance at the GIF.

References

[1] Roggero, A.; Dantras E.; Paulmier, T.; Tonon, C.; Dagras, S.; Lewandowski, S.; Payan D. *Polym. Degrad. Stab.* **2016,** *128,* 126-133.
[2] Palsule, A.; Clarson, S.; Widenhouse, C. *J. Inorg. Organomet. Polym.* **2008,** *18,* 207-221.
[3] Chien, A.; Maxwell, R.; Chambers, D.; Balazs, B.; LeMay, J. *Rad. Phys. Chem.* **2000,** *59,* 493-500.
[4] Stevenson, I.; David, L.; Gauthier, C.; Arambourg, L.; Davenas, J.; Vigier, G. *Polymer* **2001,** *42,* 9287-9292.
[5] Patel, M.; Morrell, P.; Murphy, J.; Skinner, A.; Maxwell, R. *Polym. Degrad. Stab.* **2006,** *91,* 406-413.
[6] Gillen, K.; Bernstein, R.; Celina, M. *Rubber Chem. Technol.* **2015,** *88,* 1-27.
[7] Tuckner, P. *Rubber World* **2006,** 1-6.
[8] Vondracek, P.; Schatz, M. *J. Appl. Polym. Sci.* **1979,** *23,* 2681-2694.
[9] Polmanteer, K.; Lentz C. *ACS. Sym. Proc. Rubber. Div.* **1975,** 795-809.
[10] Basfar, A. *Radiat. Phys. Chem.* **1997,** *50,* 607-610.

Appendix A: Category Plots of Analytical Data

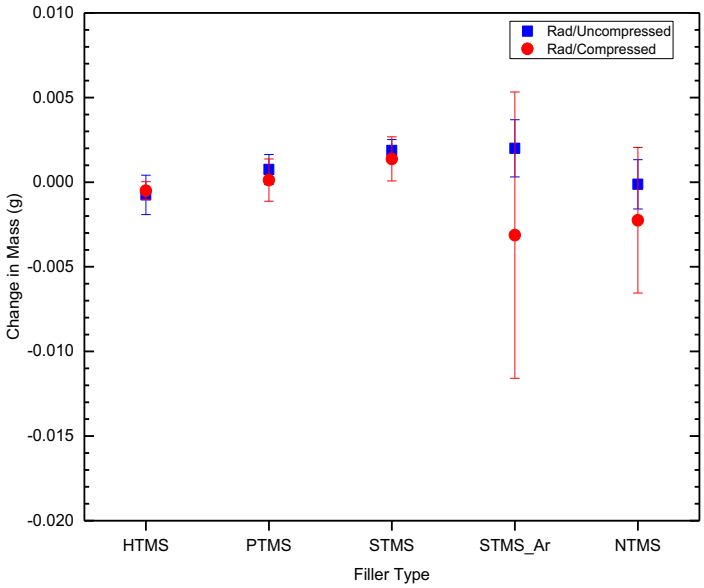

Figure A-1: Change in mass of all filled silicones tested.

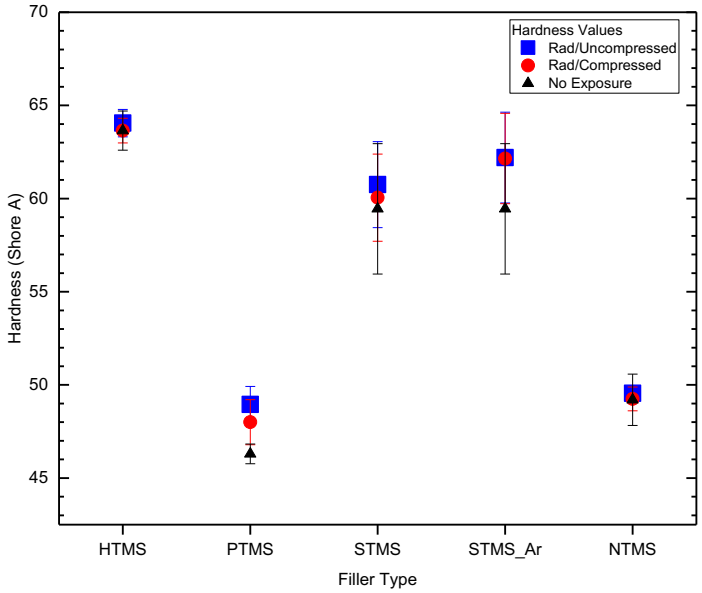

Figure A-2: Hardness of all filled silicones tested.

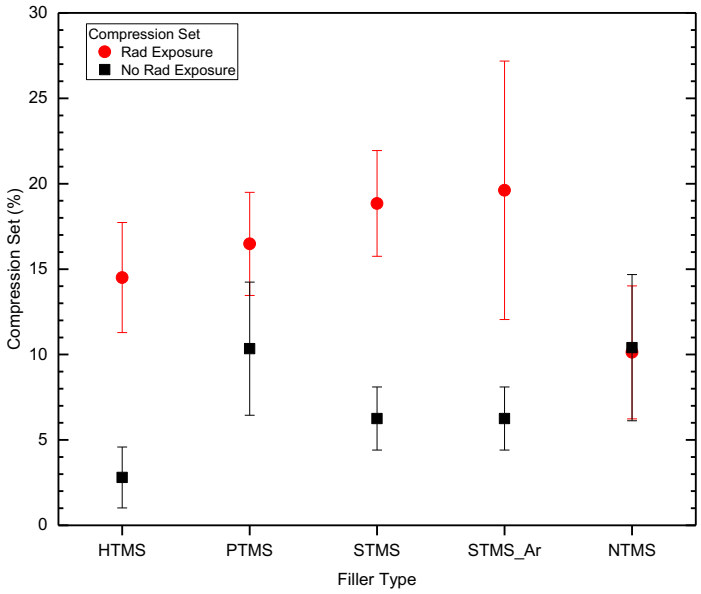

Figure A-3: Compression set data of all filled silicones tested.

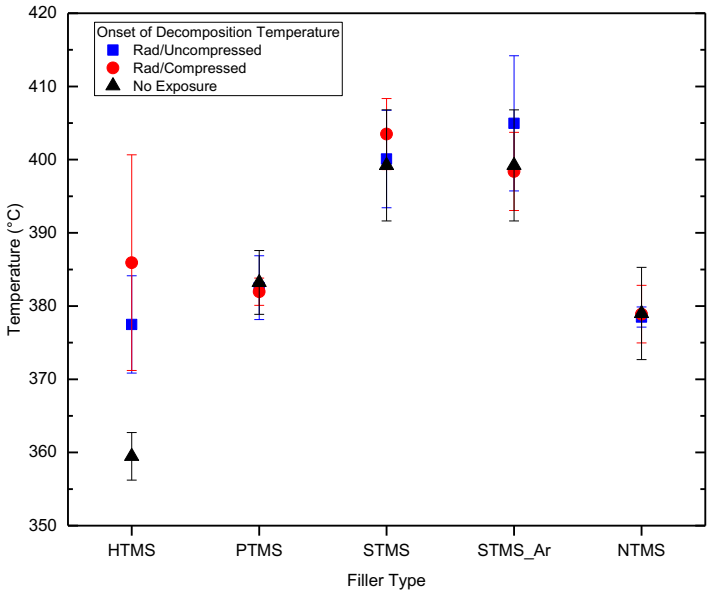

Figure A-4: TGA results; onset of decomposition temperature of all filled silicones tested.

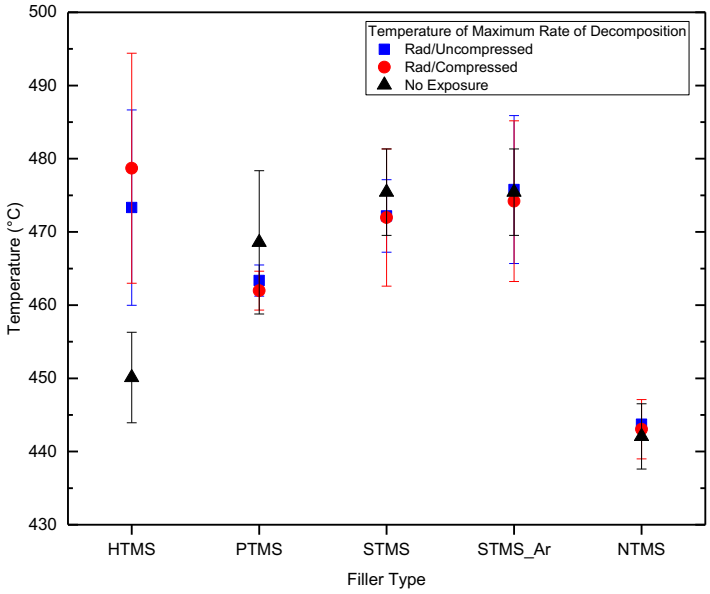

Figure A-5: TGA results; temperature of maximum rate of decomposition of all filled silicones tested.

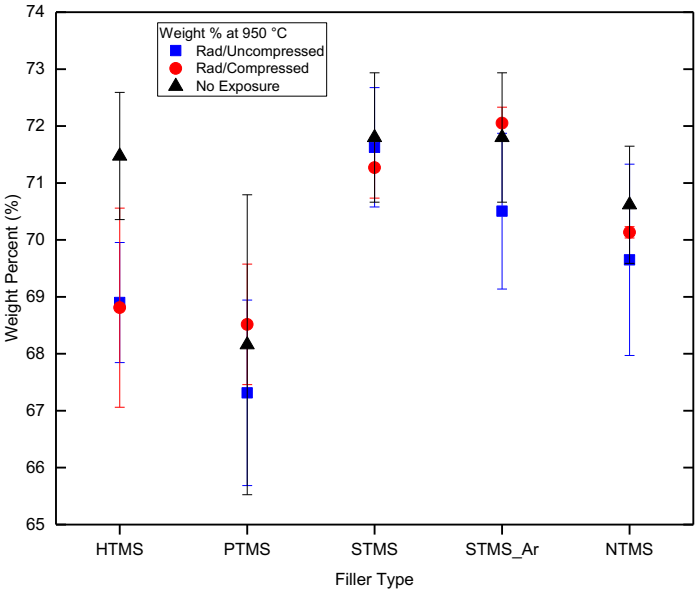

Figure A-6: TGA results; weight percent at 950 °C of all filled silicones tested.

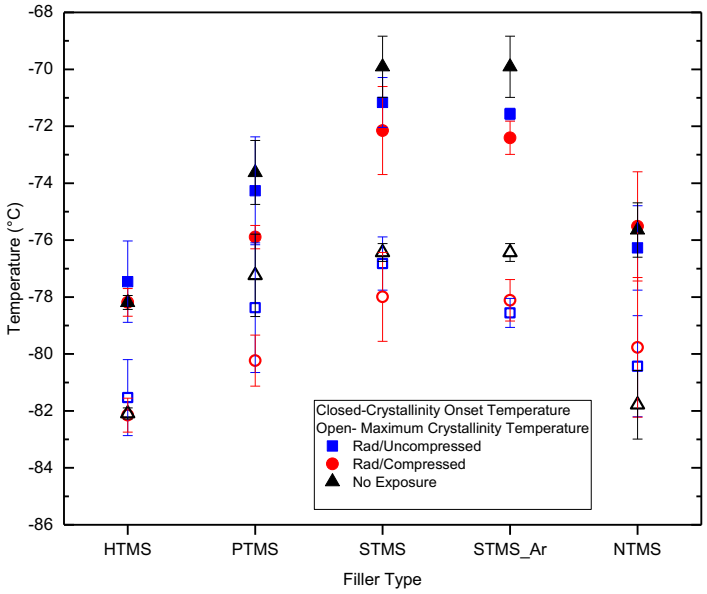

Figure A-7: DSC results; crystallinity onset and maximum temperatures of all filled silicones tested.

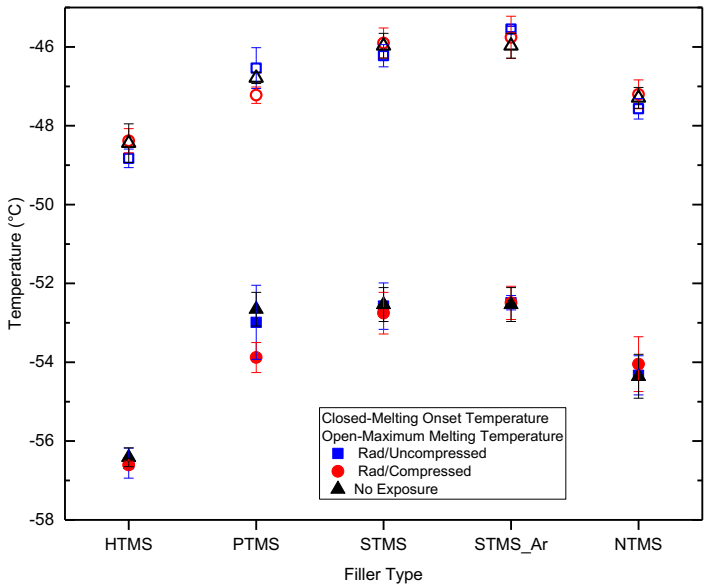

Figure A-8: DSC results; melting onset and maximum temperatures of all filled silicones tested.

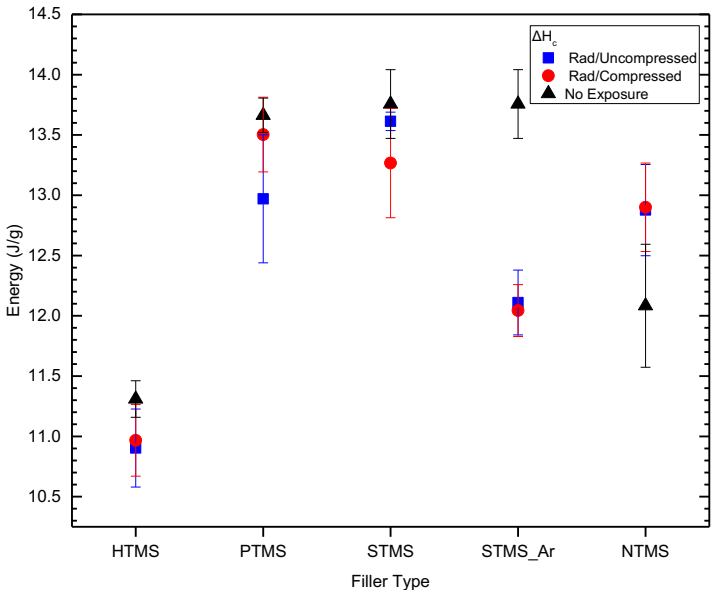

Figure A-9: DSC results; ΔH_c of all filled silicones tested.

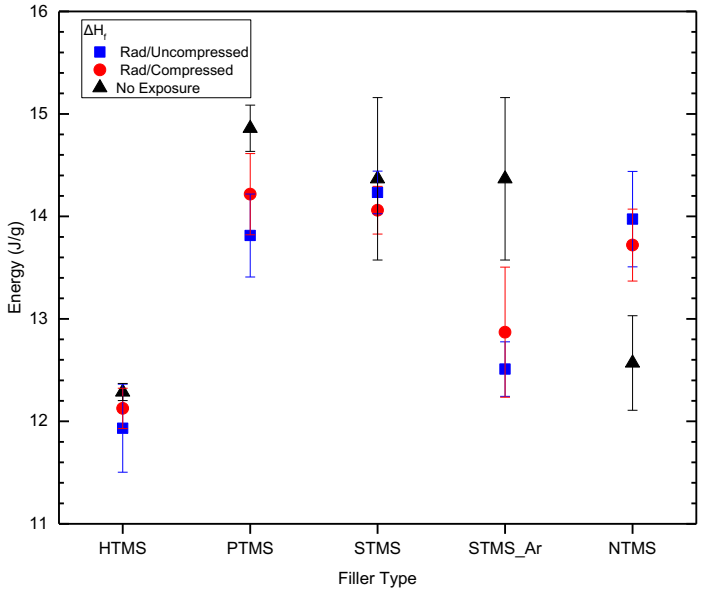

Figure A-10: DSC results; ΔH_f of all filled silicones tested

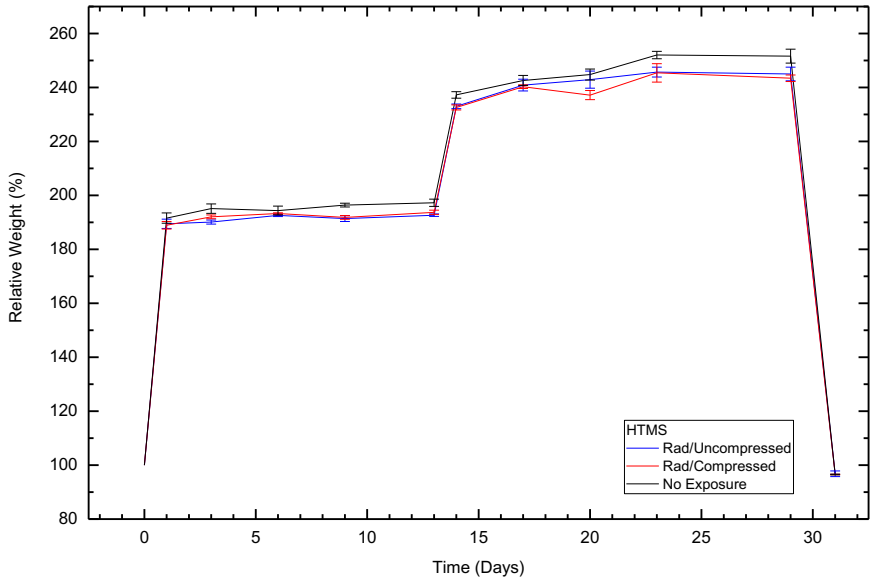

Figure A-11: Solvent swell plot of relative weight vs time of HTMS filled silicones.

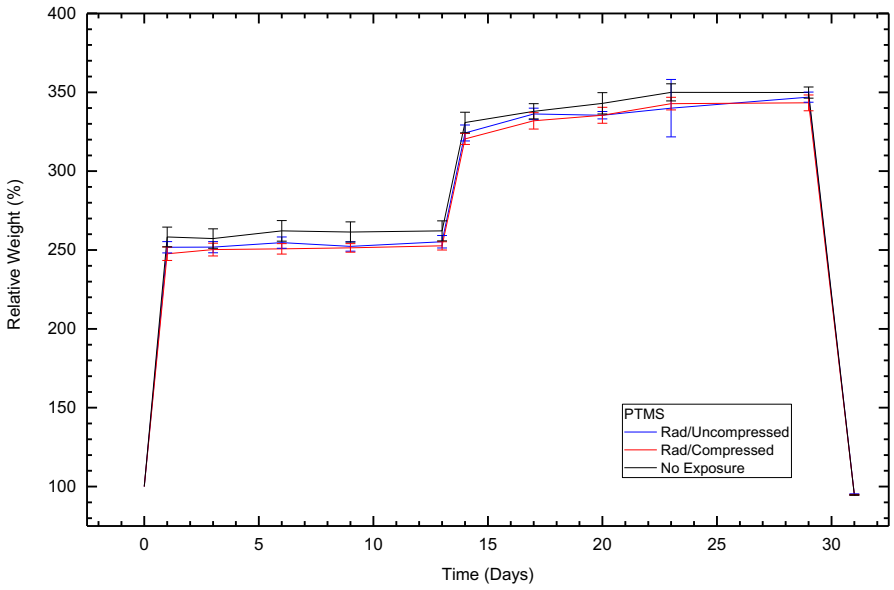

Figure A-12: Solvent swell plot of relative weight vs time of PTMS filled silicones.

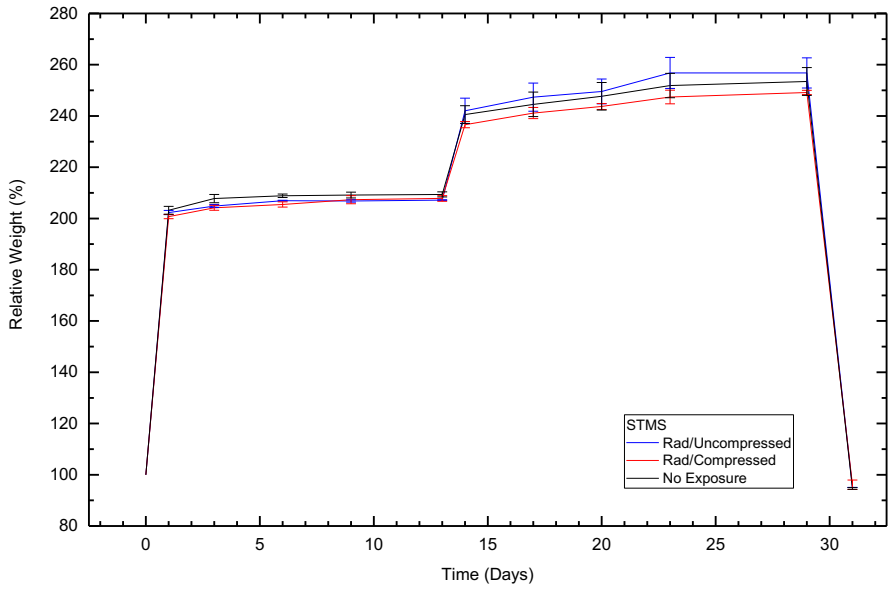

Figure A-13: Solvent swell plot of relative weight vs time of STMS filled silicones.

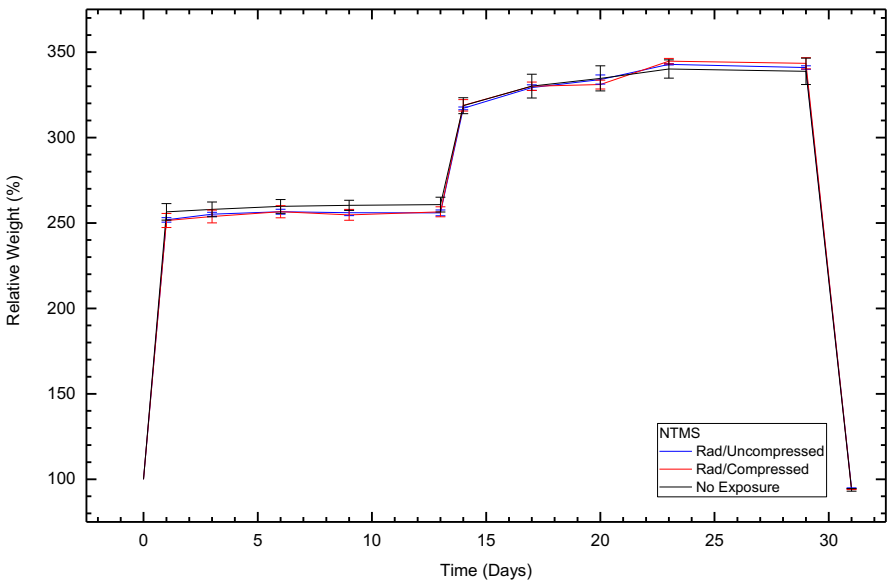

Figure A-14: Solvent swell plot of relative weight vs time of NTMS filled silicones.

Appendix B: FTIR Data of Aged and Unaged Samples

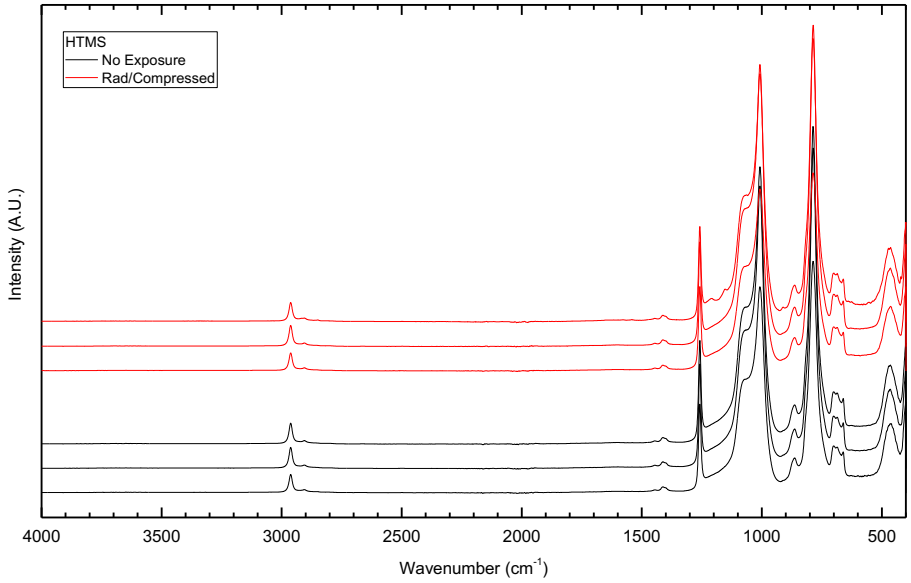

Figure B-1: IR spectra of HTMS filled silicone comparing control and radiation exposed compressed samples.

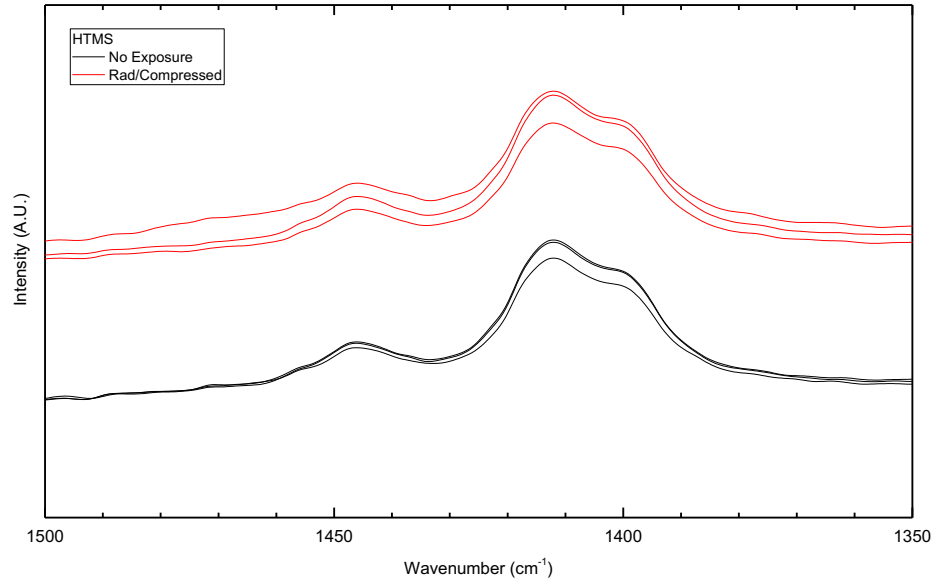

Figure B-2: Detail of IR spectra showing C=C region of HTMS filled silicone comparing control and radiation exposed compressed samples.

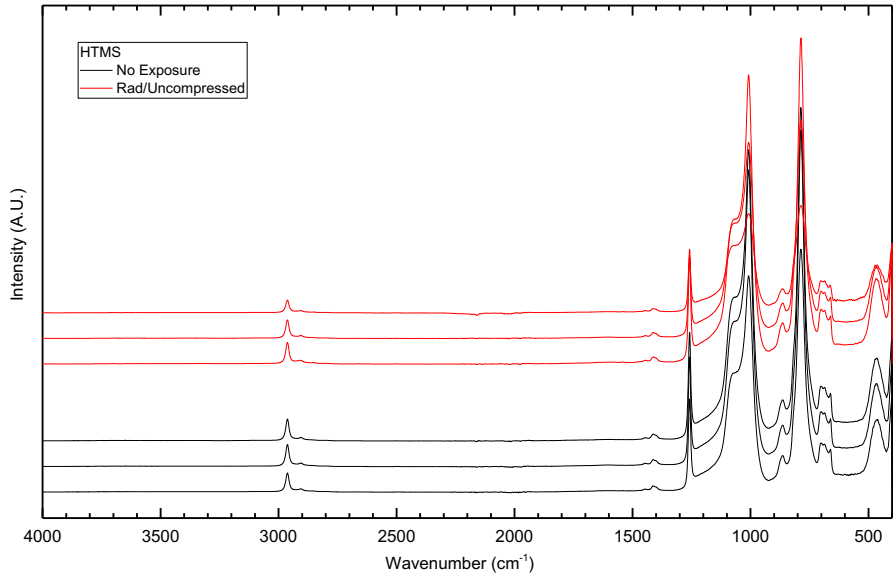

Figure B-3: IR spectra of HTMS filled silicone comparing control and radiation exposed uncompressed samples.

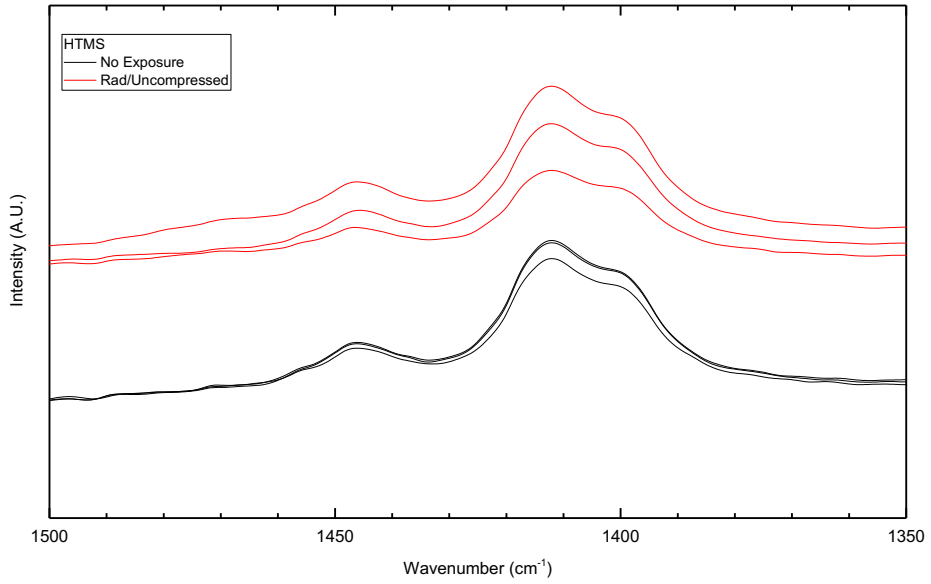

Figure B-4: Detail of IR spectra showing C=C region of HTMS filled silicone comparing control and radiation exposed uncompressed samples.

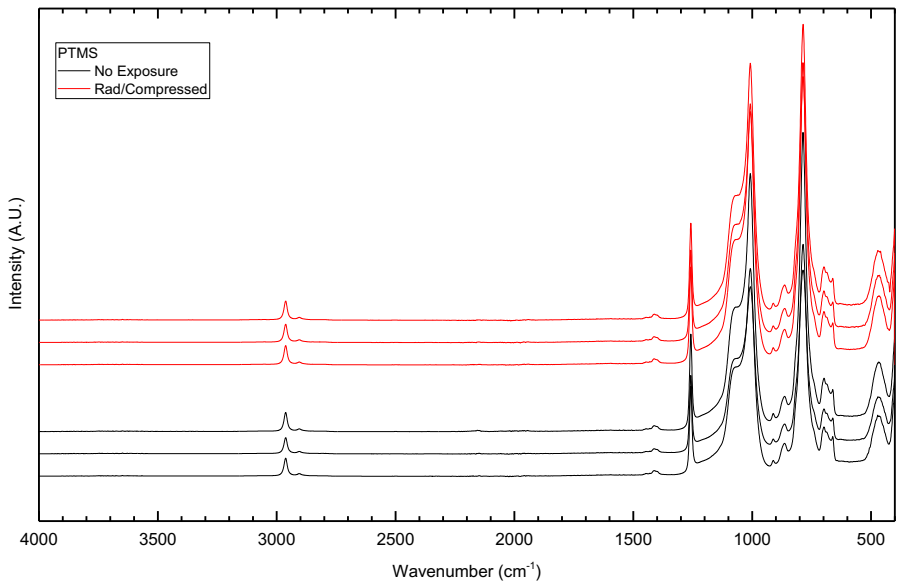

Figure B-5: IR spectra of PTMS filled silicone comparing control and radiation exposed compressed samples.

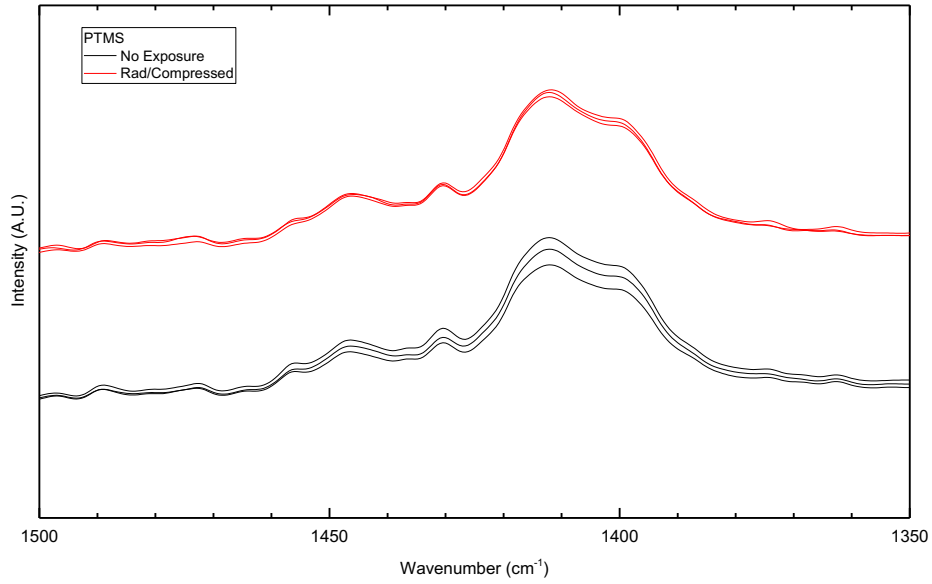

Figure B-6: Detail of IR spectra showing C=C region of PTMS filled silicone comparing control and radiation exposed compressed samples.

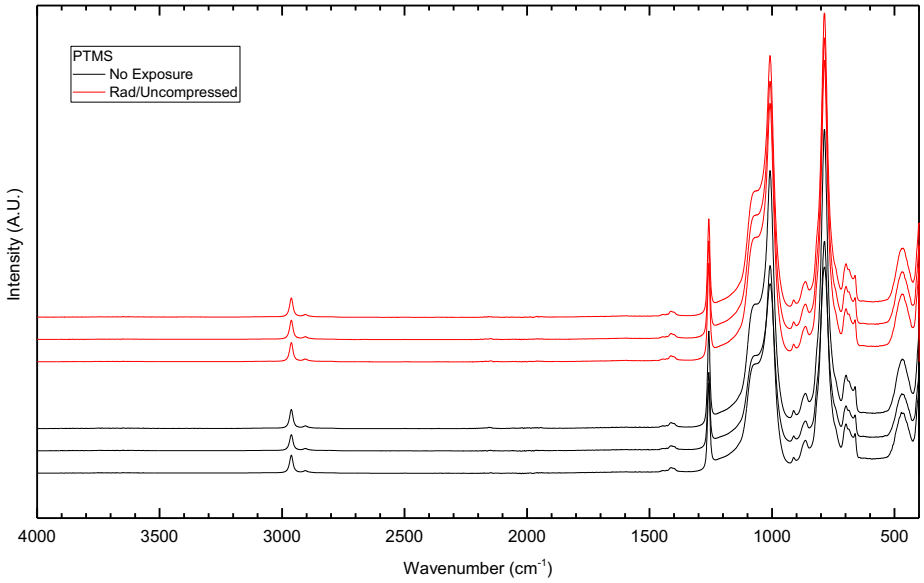

Figure B-7: IR spectra of PTMS filled silicone comparing control and radiation exposed uncompressed samples.

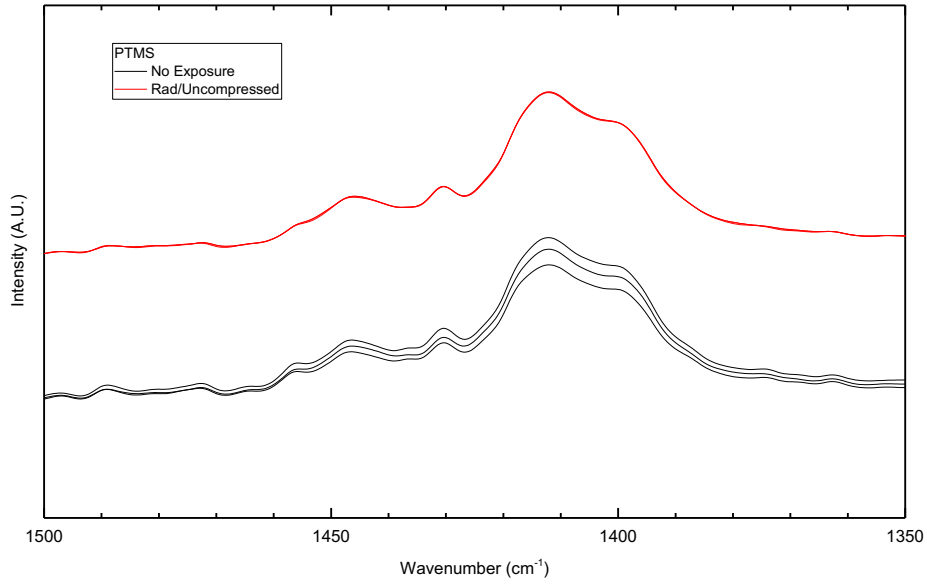

Figure B-8: Detail of IR spectra showing C=C region of PTMS filled silicone comparing control and radiation exposed uncompressed samples.

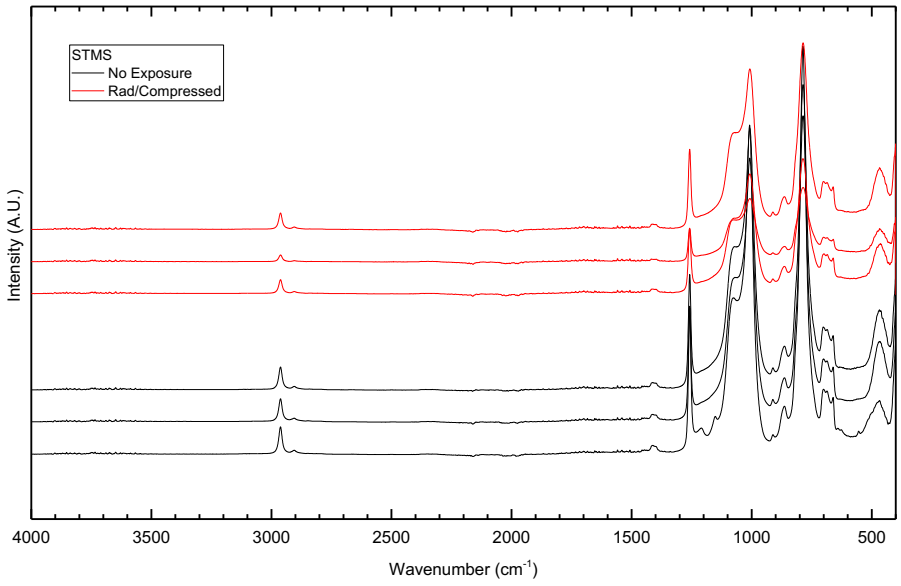

Figure B-9: IR spectra of STMS filled silicone comparing control and radiation exposed compressed samples.

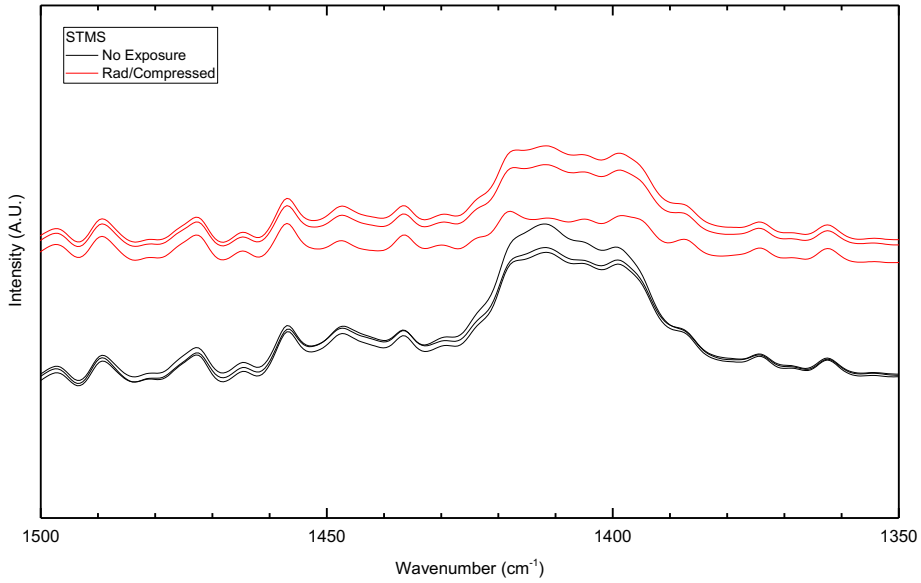

Figure B-10: Detail of IR spectra showing C=C region of STMS filled silicone comparing control and radiation exposed compressed samples.

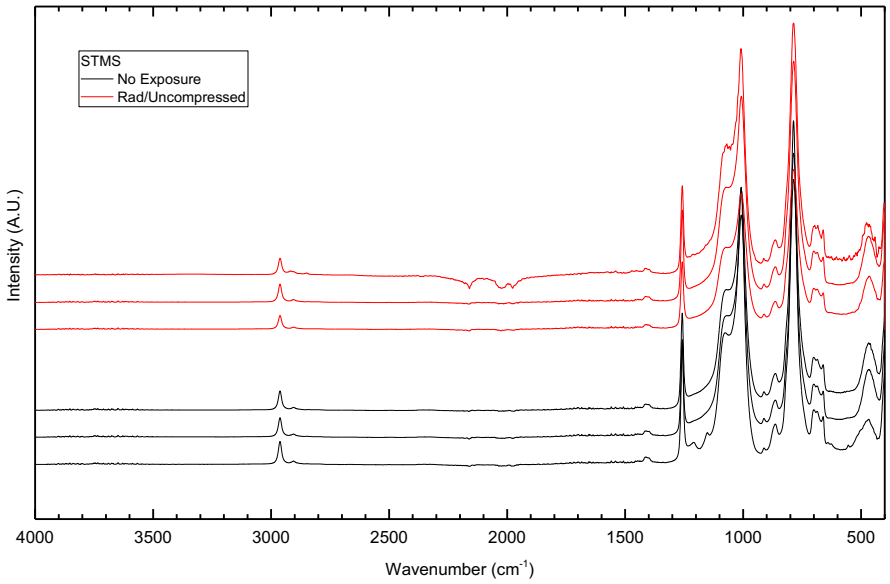

Figure B-11: IR spectra of STMS filled silicone comparing control and radiation exposed uncompressed samples.

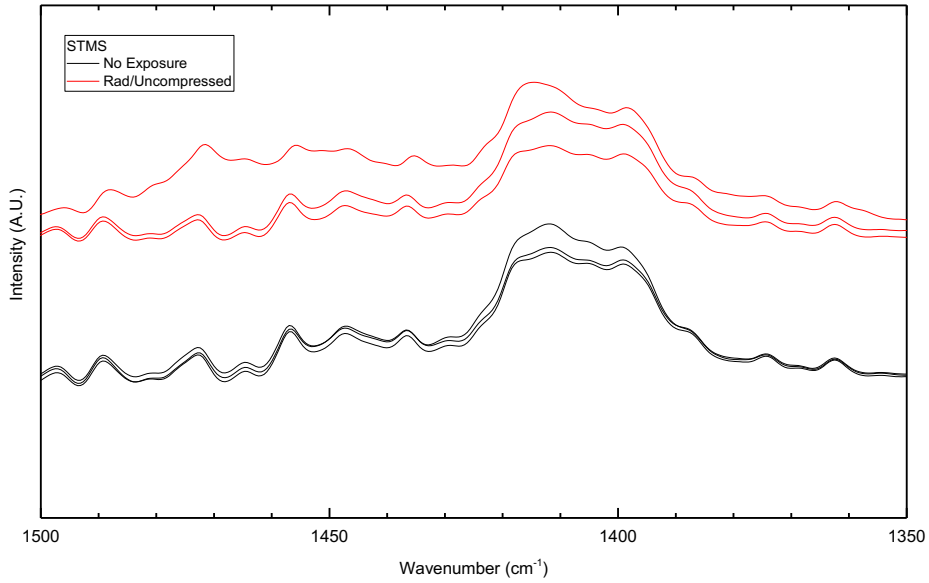

Figure B-12: Detail of IR spectra showing C=C region of STMS filled silicone comparing control and radiation exposed uncompressed samples.

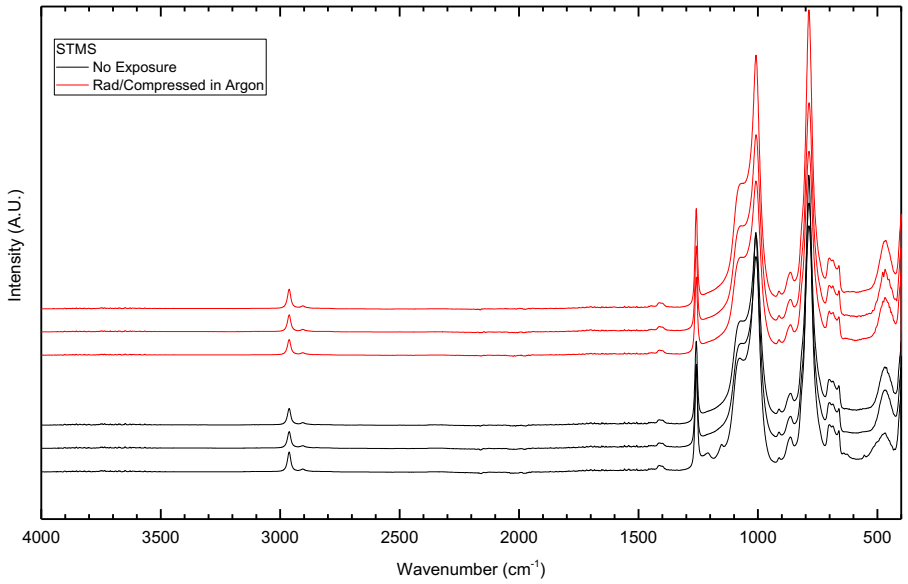

Figure B-13: IR spectra of STMS filled silicone comparing control and radiation exposed compressed samples in argon.

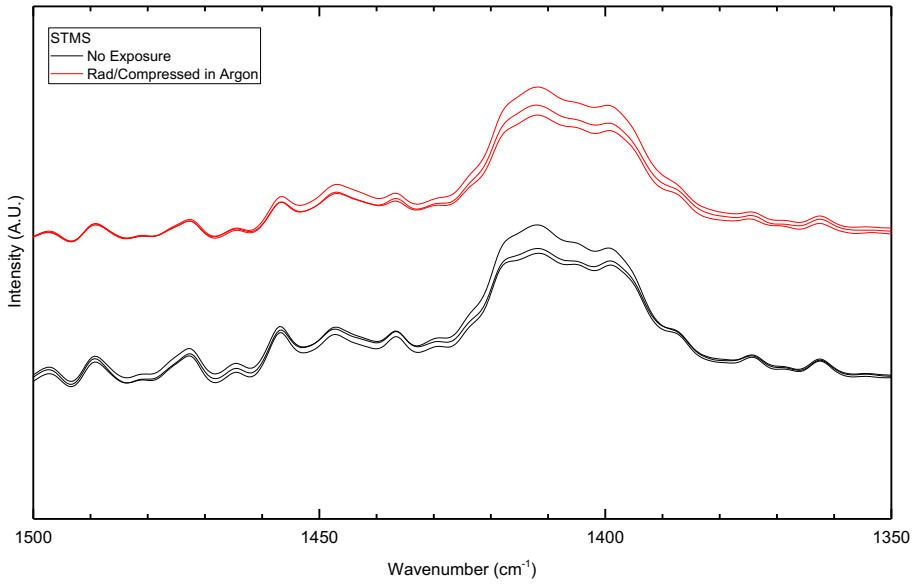

Figure B-14: Detail of IR spectra showing C=C region of STMS filled silicone comparing control and radiation exposed compressed samples in argon.

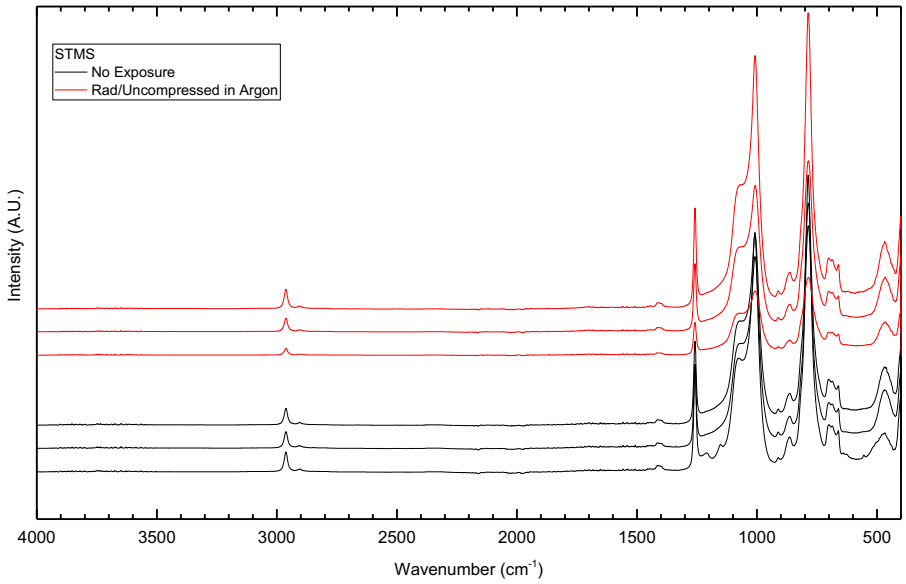

Figure B-15: IR spectra of STMS filled silicone comparing control and radiation exposed uncompressed samples in argon.

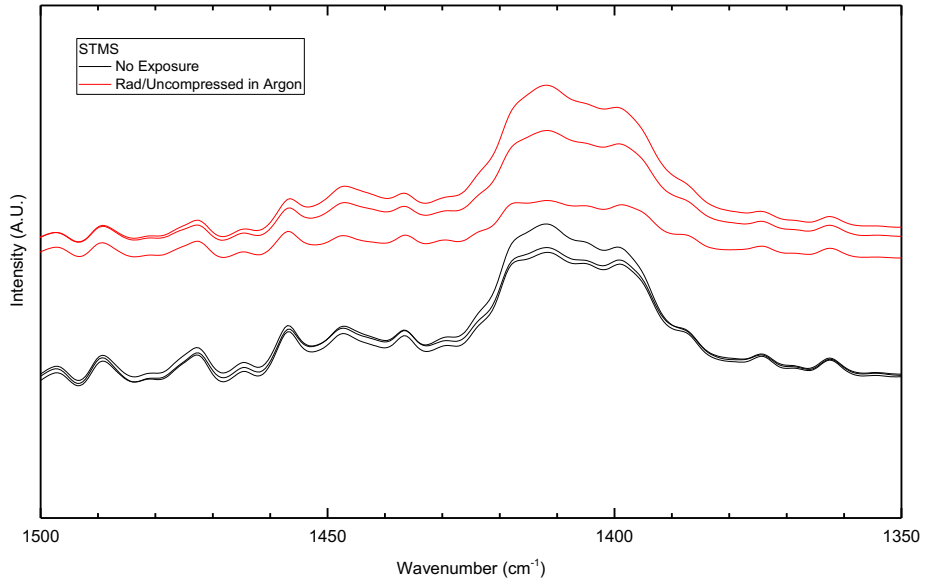

Figure B-16: Detail of IR spectra showing C=C region of STMS filled silicone comparing control and radiation exposed uncompressed samples in argon.

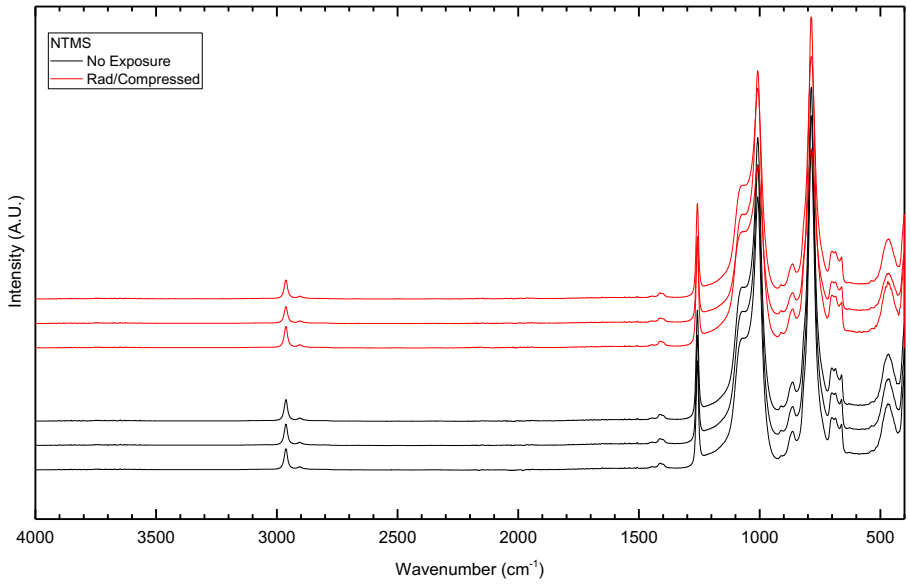

Figure B-17: IR spectra of NTMS filled silicone comparing control and radiation exposed compressed samples.

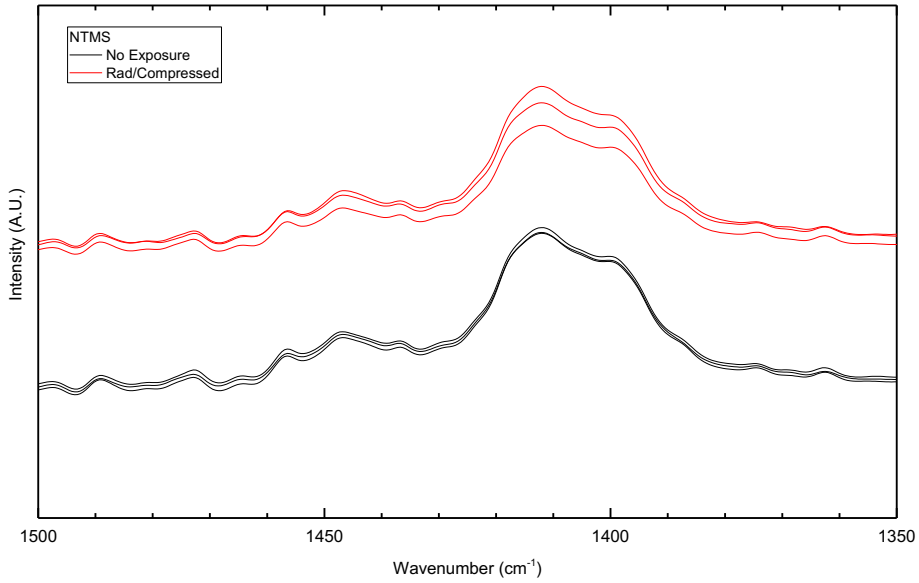

Figure B-18: Detail of IR spectra showing C=C region of NTMS filled silicone comparing control and radiation exposed compressed samples.

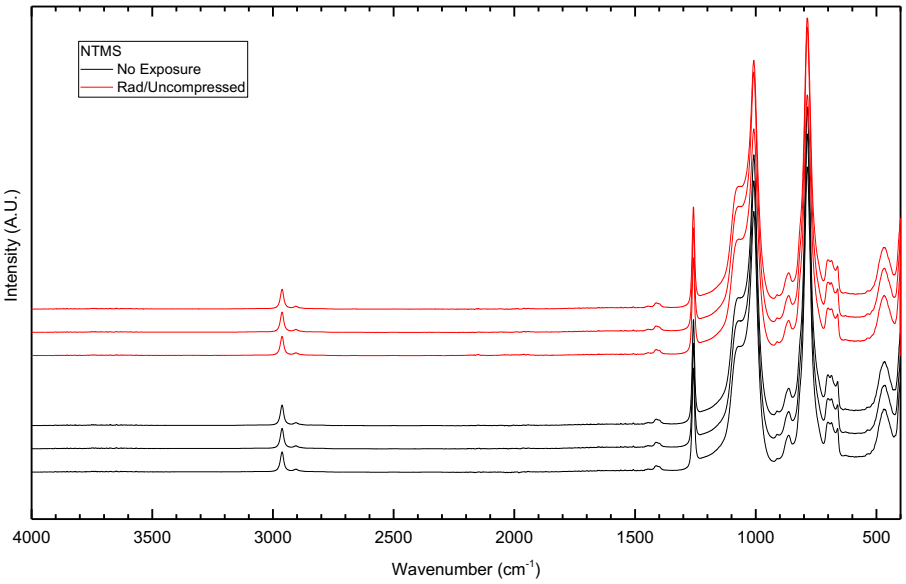

Figure B-19: IR spectra of NTMS filled silicone comparing control and radiation exposed uncompressed samples.

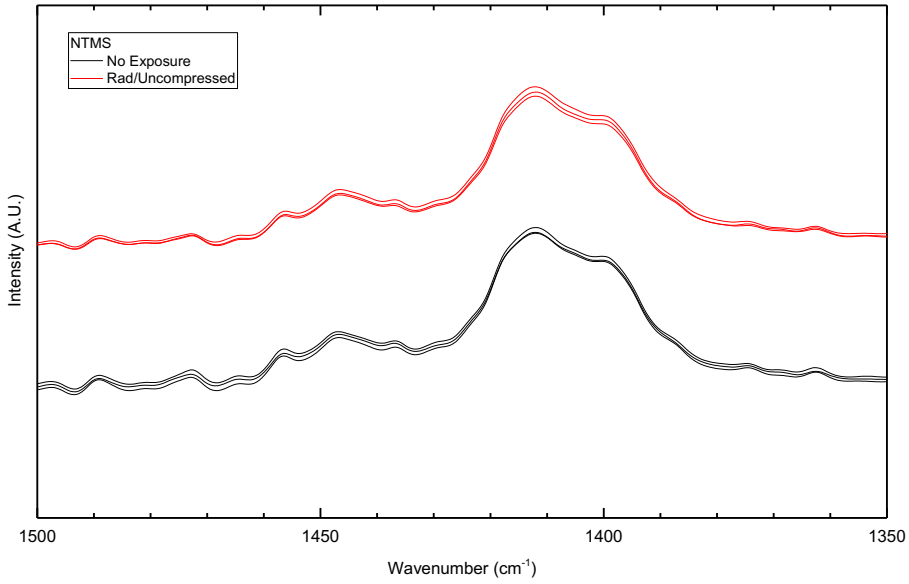

Figure B-20: Detail of IR spectra showing C=C region of NTMS filled silicone comparing control and radiation exposed uncompressed samples.